Synthesis of Poly(benzothiadiazole-*co*-dithienobenzodithiophenes) and Effect of Thiophene Insertion for High-Performance Polymer Solar Cells

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Abstract: We describe herein the synthesis of novel donor–acceptor conjugated polymers with dithienobenzodithiophenes (DTBDT) as the electron donor and 2,1,3-benzothiadiazole as the electron acceptor for high-performance organic photovoltaics (OPVs). We studied the effects of strategically inserting thiophene into the DTBDT as a substituent on the skeletal structure on the opto-electronic performances of fabricated devices. From UV/Vis absorption, electrochemical, and fieldeffect transistor analyses, we found that the thiophene-containing DTBDT derivative can substantially increase the orbital overlap area between adjacent conjugated chains and thus dramatically enhance charge-carrier mobility up to $0.55 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$. The outstanding

Keywords: copolymerization • donor-acceptor systems • photovoltaic systems • thin films • semiconductors charge-transport characteristics of this polymer allowed the realization of high-performance organic solar cells with a power conversion efficiency (PCE) of 5.1%. Detailed studies on the morphological factors that enable the maximum PCE of the polymer solar cells are discussed along with a hole/electron mobility analysis based on the space-charge-limited current model.

Introduction

Conjugated polymer bulk heterojunction (BHJ) solar cells consisting of an electron-rich conjugated polymer and an electron-deficient fullerene placed between suitable electrodes have attracted considerable attention during the last decade and power conversion efficiencies (PCEs) of 10% have now been achieved.^[1-4] In most cases, [6,6]phenyl-C₆₁butyric acid methyl ester (PC₆₁BM) or [6,6]phenyl-C₇₁-butyric acid methyl ester (PC₇₁BM) have shown the best performance as acceptors in BHJ solar cells, and there is little room for further chemical modification of these two fullerene derivatives. However, in the case of polymers used as donors in BHJ solar cells, various synthetic strategies have proved effective in enhancing light-harvesting ability, exci-

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ton dissociation and/or diffusion, and charge extraction, resulting in increased PCEs of solar cells.^[5–10] Thus, the molecular design of new conjugated polymers remains one of the most important issues for organic photovoltaics (OPVs).

In this regard, it is well known that the energy levels of polymers should be optimized to obtain a low band-gap while maintaining the driving force for charge separation. On this basis, research groups have extensively developed conjugated polymers with alternating donor-acceptor (D–A) units to tune the energy levels by controlling the intramolecular charge transfer (ICT) from the donor to the acceptor moiety.^[10-15]

Among the various D-A conjugated polymers, benzo[1,2b:4,5-b']dithiophene (BDT) has been widely used as the donor unit for high-performance OPVs.^[16-19] For example, the copolymerization of BDT with various acceptor units, such as thieno[3,4-b]thiophene (TT),^[17] thiophene-TT,^[18] and *N*-alkylthieno[3,4-c]pyrrole-4,6-dione (TPD),^[19] has led to BDT-based conjugated polymers showing promising OPV performances. Furthermore, fused derivatives of BDT, such as dithieno[2,3-d:2',3'-d']benzo[1,2-b:4,5-b']dithiophene (DTBDT), as donor units in polymers have also shown reasonably high PCEs when combined with TT as an acceptor unit.^[20,21] These kinds of linearly fused aromatic rings often introduce superior intermolecular charge-transport properties due to the planarity of the backbone and there have been many reports on the high charge-carrier mobility of these moieties when employed as organic field-effect transistors.^[22]

In this paper we report on the synthesis of novel D-A conjugated polymers with DTBDT as the electron donor

and 370°C, respectively (see Figures S1 and S2 in the Sup-

To demonstrate the electronic structures as well as the

molecular energy levels of PDTBDAT-BZ and PDTBDOR-

BZ, the UV/Vis absorption spectra of both polymers in solu-

tion and as thin films are shown in Figure 1 and the corre-

sponding data in Table 1. Notably, thermal annealing of the

thin films did not lead to many changes in either the shape

or intensity of the thin-film absorption spectra (not shown).

By using the UV/Vis data combined with electrochemical

data (see Figure S3 in the Supporting Information), the

and 2,1,3-benzothiadiazole (BT) as the electron acceptor for high-performance OPVs (Scheme 1). PDTBDAT-BZ, with two thiophene units strategically incorporated as substituents into DTBDT, is expected to show enlarged π overlap between adjacent polymer chains and thus enhanced intermolecular charge-transport characteristics compared with PDTBDOR-BZ. As a result, PDTBDAT-BZ shows a relatively high field-effect mobility of 0.55 cm²V⁻¹s⁻¹, which is a significant value among BDT derivatives. Optimized OPVs based on PDTBDAT-BZ revealed a high PCE of 5.1%. A systematic analysis of the chemical, optical, and electrochemical properties of these polymers as well as of various opto-electronic characteristics, such as transistor, OPV, and space-charge limited current (SCLC) properties, was carried out to explain the high per-

formance of PDTBDAT-BZ as a donor material.

Results and Discussion

The strategies for the synthesis of PDTBDAT-BZ and PDTBDOR-BZ are presented in Scheme 1 and in the Experimental Section. Both polymers exhibit good thermal stability, showing less than 5% weight loss at temperatures up to 400



porting Information).

Figure 1. Normalized UV/Vis absorption spectra of a) PDTBDAT-BZ and b) PDTBDOR-BZ.

900

1000

400

500

600

700

Wavelength (nm)

800

900

1000



400

500

600

700

Wavelength (nm)

800

Scheme 1. Synthetic routes to the polymers PDTBDAT-BZ and PDTBDOR-BZ. All the details of the reactions can be found in the Experimental Section.

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- 13243

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Table 1. Energy levels of the PDTBAT-BZ and PDTBDOR-BZ polymers based on UV/Vis absorption and electrochemical data.

| | $\lambda_{max,S}$ | $\lambda_{max,F}$ | Band gap (optical) | LUMO (optical) | HOMO (electrochemical) |
|------------|-------------------|-------------------|-----------------------|-------------------|---------------------------|
| | [nm] | [nm] | [eV] | [eV] | [eV] |
| PDTBDAT-BZ | 660 | 670 | | | |
| | 420 | 425 | 1.59 | 3.85 | 5.44 |
| | 341 | 344 | | | |
| PDTBDOR-BZ | 673 | 696 | 1 55 | 3 79 | 5 34 |
| | 409 | 413 | 1.00 | 5.17 | 5.51 |

separation when blended with PCBM. The absorption maximum of PDTBDOR-BZ is redshifted compared with that of PDTBDAT-BZ by more than 10 nm in both solution and thin films. This can be attributed to more localized charge carriers in thiophene-substituted DTBDT, which can partially inhibit ICT from the donor to acceptor unit. Another interesting difference between the two polymers is the shape of the thin-film absorption spectra. It is clear that the thinfilm absorption spectrum of PDTBDAT-BZ has a distinct shoulder-like feature at around 610 nm, which is absent in the corresponding spectrum of PDTBDOR-BZ. This shoulder-like feature grows as a result of solidification or increased aggregation of the polymer chain of PDTBDAT-BZ. In conjugated polymers, this often indicates strong intermolecular packing in the solid state and, in our present cases,^[23,24] it can be attributed to the more planar and rigid backbone of PDTBDAT-BZ in comparison with that of PDTBDOR-BZ.

To support these findings, the charge-transport behavior of the two polymers was compared by using a bottom gate/top contact transistor geometry. From the transfer characteristics measured in the saturation regime, it is apparent that PDTBDAT-BZ has superior charge-transport behavior, or higher charge-carrier mobility. By using well-known *I–V* expressions in such transistor geometry, the

field-effect mobility was determined to be $0.55 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for PDTBDAT-BZ and $0.001 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$ for PDTBDOR-BZ. Thermal annealing in the temperature range 50–200 °C did not lead to any notable enhancement in the charge-carrier mobility, which is consistent with the results obtained by UV/Vis absorption measurements. The output characteristics of these devices also showed huge differences in current, as shown in Figure 2b,c. To the best of our knowledge, the field-effect mobility of PDTBDAT-BZ ($0.55 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$) is the highest value known for BDT-based polymers. Therefore it is reasonable to conclude that PDTBDAT-BZ has a more efficient intermolecular packing structure and thus higher charge-carrier mobility as a result of the thiophene units strategically incorporated onto the side of the backbone.



Figure 2. a) Transfer characteristics of transistors based on PDTBDAT-BZ and PDTBDOR-BZ. The output characteristics of (b) PDTBDAT-BZ and (c) PDTBDOR-BZ based transistors; the traces for 0 V and 6 V overlap.

13244 -

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Chem. Eur. J. 2013, 19, 13242-13248

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To investigate the photovoltaic properties of PDTBDAT-BZ and PDTBDOR-BZ, organic solar cell (OSC) devices were fabricated and characterized. Under typical OSC fabrication conditions without any pre- or post-treatment, PDTBDAT-BZ routinely showed 1.5-1.7% PCE depending on the blending ratio with PCBM. In the case of PDTBDOR-BZ, the PCEs of the OPVs were slightly lower, 1.1-1.4%, depending on the device fabrication conditions (see Table S1 in the Supporting Information). Many researchers have recently shown that a suitable post-treatment process can induce a favorable morphology of the BHJ films, resulting in a dramatically enhanced PCE in comparison with pristine OPVs. The most widely studied post-treatment is thermal annealing, which enables the self-organization of crystalline semiconductors and leads to a phase-separated nanomorphology.^[25-28] Slow drying processes or solvent annealing methods have also yielded enhanced photovoltaic performances by mechanisms similar to that of thermal annealing.^[29] The addition of processing additives to the blend solution is an especially promising method for enhancing the performances of the resulting devices^[30-34] because the fabrication process occurs in a single step rather than in two steps (including thermal annealing), and less time is required than for solvent annealing. For example, incorporating a small amount of alkanedithiol into solutions yielded dramatic increases in the PCEs of PCPDTBT/PC71BM-[33] and P3HT/PCBM^[34]-based BHJ photovoltaic devices. In the aforementioned reports, the authors reasoned that the improved photovoltaic performance resulted from a more extensively phase-separated morphology, with domain sizes that exceed several tens of nanometers due to the increased crystallinity of the components. Given this background, we have also explored various post-optimization processes for OSCs developed by our group and found that the addition of a processing additive, especially 1,8-diiodooctane (DIO), to a blend solution is the most efficient method for enhancing OPV performances. As summarized in Table 2, the short circuit current (J_{SC}) and fill factor (FF) of OPVs based on PDTBDAT-BZ are increased by more than 100 and 64%, respectively, after the incorporation of this additive. The OPVs data (absence of the additive (DIO)) were added to

Table 2. Photovoltaic characteristics of PDTBDAT-BZ- and PDTBDOR-BZ-based OPVs under various optimization conditions.

| Polymer | Spin rate | P/PCBM ^[a] | $V_{\rm oc}$ | $J_{\rm SC}$ | FF | PCE |
|------------|-----------|-----------------------|--------------|----------------|-------|------|
| | - | | [V] | $[mA cm^{-2}]$ | [%] | [%] |
| PDTBDAT-BZ | 2000 | 1:2 | 0.80 | 8.14 | 68.23 | 4.45 |
| | 3000 | 1:2 | 0.81 | 8.67 | 69.57 | 4.91 |
| | 2000 | 1:3 | 0.80 | 8.66 | 67.38 | 4.68 |
| | 3000 | 1:3 | 0.80 | 9.38 | 67.81 | 5.10 |
| | 2000 | 1:4 | 0.80 | 9.31 | 64.06 | 4.80 |
| | 3000 | 1:4 | 0.80 | 9.56 | 63.21 | 4.80 |
| PDTBDOR-BZ | 2000 | 1:2 | 0.61 | 5.44 | 47.81 | 1.61 |
| | 3000 | 1:2 | 0.61 | 5.54 | 48.60 | 1.66 |
| | 2000 | 1:3 | 0.62 | 6.36 | 48.10 | 1.91 |
| | 3000 | 1:3 | 0.62 | 5.22 | 53.67 | 1.74 |

[a] Polymer/PC71BM blends with additive (DIO 2%).

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with and without DIO as additive.

- 13245

Supporting Information Table S1. and the PCE of the best device is 5.1%. Although OPVs based on PDTBDOR-BZ also show enhanced performances as a result of using an additive, the magnitudes of the increase are much lower than for PDTBDAT-BZ, with the best device having a PCE of 1.9% despite tremendous efforts at device optimization. This may be related to the relatively poor intermolecular π orbital overlap in PDTBDOR-BZ and thus the limited effect of the addition of the additive compared with PDTBDAT-BZ, which has thiophene units incorporated on to the skeleton. The lower $V_{\rm OC}$ of PDTBDOR-BZ compared with PDTBDAT-BZ can be understood in terms of the relative positions of the HOMOs, 5.34 and 5.44 eV, respectively. The *I*-V curves of the best devices prepared from each polymer are shown in Figure 3 along with the corresponding external quantum efficiency (EQE) spectra.



Figure 3. (a) I-V characteristics of the devices with DIO as processing additive and (b) EQE curves of the corresponding OSCs.

X-ray diffraction analysis of the thin films was performed to study the effect of the additive DIO on PDTBDAT-BZbased BHJ films (Figure 4). The Bragg diffraction feature corresponding to the (100) crystalline plane of the polymer lamellar stacks clearly increases after addition of the processing additive, which demonstrates that the incorporation of the additive is effective in the PDTBDAT-BZ/PC₇₁BM blend system (for atomic force microscopy (AFM) images, see Figure S4 in the Supporting Information).



The hole and electron mobility in the blends of polymers and PCBM were measured and analyzed by using the SCLC method to elucidate the mechanism by which the photovoltaic performance of PDTBDAT-BZ-based OPVs is dramatically enhanced in the presence of a processing additive. As shown in Figure 5and Table 3, in the case of hole charge car-



Figure 5. *I–V* characteristics of the SCLC measurement of PDTBDAT-BZ:PC $_{71}$ BM blend with and without DIO

Table 3. Photovoltaic characteristics of PDTBDAT-BZ-based OPVs under various conditions.

| Polymer | Hole mobility $[cm^2 V^{-1}S^{-1}]$ | Electron mobility $[cm^2V^{-1}S^{-1}]$ | $\mu_{ m e}/\mu_{ m h}$ | PCE [%] | |
|--|-------------------------------------|--|-------------------------|------------|--|
| PDTBDAT-BZ/PC ₇₁ BM (1:2) without DIO | 2.40×10^{-5} | 1.36×10^{-8} | 1986.2 | 1.70 | |
| PDTBDAT-BZ/PC ₇₁ BM | 8.56×10^{-6} | 2.46×10^{-6} | 3.47 | 4.91 | |
| (1:2) with 2% DIO PDTBDAT-BZ/PC ₇₁ BM | 6.35×10^{-6} | 2.46×10^{-6} | 2.7 | 5.10 | |
| (1:3) with 2% DIO PDTBDAT-BZ/PC ₇₁ BM (1:4) with 2% DIO | 4.70×10^{-6} | 4.73×10^{-6} | 1.007 | 4.8 | |

riers, PDTBDAT-BZ/PC₇₁BM blends with and without the processing additive provide hole mobility in the order of 10^{-6} and 10^{-5} cm²V⁻¹s⁻¹, respectively. The difference is far less than an order of magnitude, which indicates that the superior hole-transporting ability of PDTBDAT-BZ enables high hole mobility in BHJ films even in the absence of processing additives.

Conclusion

Novel donor-acceptor conjugated polymers with dithienobenzodithiophenes (DTBDT) as the electron donor and 2,1,3-benzothiadiazole as the electron acceptor have been synthesized. Following the design strategy of extending the area of delocalized π electrons along the polymer backbone, thiophene units were incorporated as substituents on to the skeletal structure of DTBDT to form PDTBDAT-BZ. The chemical and photophysical properties of PDTBDAT-BZ were systematically studied and compared with those of a similar DTBDT derivative with alkoxy substituents (PDTBDOR-BZ). The extended π conjugation in PDTBDAT-BZ led to an impressively high charge-carrier mobility of up to $0.55 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1}$, which is more than two orders of magnitude greater than that of PDTBDOR-BZ. The outstanding charge-transport characteristics of PDTBDAT-BZ led to high-performance organic solar cells with a PCE of 5.1% in the presence of a processing additive. An X-ray diffraction study combined with a SCLC analysis revealed that the processing additive enables phase separation of the BHJ film and thus an optimum balance between hole and electron charge-carrier mobility.

Experimental Section

Product characterization: ¹H and ¹³C NMR spectra were recorded with a Bruker Avance-300 spectrometer. Thermal analysis was performed on a TA TGA 2100 thermogravimetric analyzer under a nitrogen atmosphere at a heating rate of 10 °Cmin⁻¹. Differential scanning calorimetry (DSC) was conducted under nitrogen on a TA 2100 DSC instrument. Samples were heated at 10 °Cmin⁻¹ from 30 to 300 °C. UV/Vis absorption spectra were recorded with a UV-1650PC spectrophotometer. The molecular weights and polydispersities of the copolymers were determined by gel permeation chromatography (GPC) analysis with polystyrene used for standard calibration (waters high-pressure GPC assembly Model M515

pump, u-Styragel columns of HR4, HR4E, HR5E, with 500 and 100 Å, refractive index detectors, solvent THF). Cyclic voltammetry (CV) was performed on an EG and G Parc model 273 Å potentiostat/galvanostat system with a three-electrode cell in a solution of 0.1 м tetrabutylammonium perchlorate (Bu₄NClO₄) in acetonitrile at a scan rate of 50 mV s⁻¹. The polymer films were coated on a square carbon electrode by dipping the electrode into the corresponding solvents and then dried under nitrogen. A platinum wire was used as the counter electrode and an $Ag/AgNO_3$ (0.1 M) electrode as the

reference electrode. Atomic force microscopy (AFM) was performed with an XE-100 Advanced Scanning Probe Microscope operating in noncontact mode to image the surface morphology. Wide-angle X-ray diffraction (XRD) measurements were performed at room temperature with a D8 DISCOVER spectrometer with a general area detector. diffraction system (GADDS, Bruker AXS).

Transistor fabrication: Cytop (AGC) was deposited on SiO₂ (100 nm) to tune the dielectric surface to a more hydrophobic one. (water contact angle >108°) The thicknesses of the Cytop film were determined by using an ellipsometer (J. A. Woollam. Co. Inc.) to be less than 10 nm. The capacitance measurements were performed by using an SR 720 LCR meter at frequencies ranging from 100 Hz to 100 kHz. The capacitance measured at 100–120 Hz, 32 nF cm⁻², was used to determine the mobility. A thermally evaporated gold electrode (>60 nm) was used as source-drain electrode to construct a 100 µm channel top/contact bottom-gate transistor. The transfer and output characteristics of the transistor were measured in air by using Keithley 2400 and 236 source and measuring units.

OPV device fabrication: Organic photovoltaic cells were fabricated using the structure ITO/PEDOT–PSS/conjugated polymer–PC₇₁BM/LiF/Al. The glass substrate with pre-patterned ITO (active layer of 0.06 mm^2) was subjected to ultrasound in detergent, deionized water, CMOS-grade acetone, and isopropyl alcohol, and the surface of the glass substrate was modified by UV/ozone treatment for 20 min. Poly(3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT/PSS; Baytron PVP AI4083, Bayer AG) as hole injection material was spin-coated at 4000 rpm for

13246 ·

50 s to give a thickness of 30-40 nm on the cleaned ITO-patterned glass substrate after filtration using a 0.45 µm filter followed by baking in an oven at 120°C for more than an hour. PC71BM, a fullerene derivative (99.5%), as the electron acceptor was obtained from NanoC. The various concentration ratios of conjugated polymers to PC71BM (1:2, 1:3, or 1:4 weight ratio) in chlorobenzene (2 or 3% DIO) were prepared to yield 10 mg mL⁻¹ solutions that were stirred in a glovebox overnight under a nitrogen atmosphere. The blended solutions were spin-coated at 2000 rpm for 60 s to give a thickness of 120 nm on the top of the PEDOT/PSS layer in the glovebox. The LiF and aluminium cathodes were thermally deposited to give thicknesses of 0.8 and 100 nm, respectively, on the surface of the active layer. The current density-voltage (J-V) characteristics were measured by using a Keithley 2400 source measurement unit in the dark and under AM 1.5 G solar illumination (Zolix SS150A solar simulator) with respect to a reference cell PVM 132 calibrated at the National Renewable Energy Laboratory at an intensity of 100 mW cm⁻². The incident photon to charge carrier efficiency (IPCE) was determined by using a certified IPCE instrument (Zolix Instruments, Inc, SolarCellScan100).

Polymer synthesis: All reactions were carried out under a nitrogen atmosphere by using the usual Schlenk techniques. All chemical reagents were purchased from Aldrich and used as received. Other chemicals were used unless otherwise specified. 3-Bromothieno[3,2-*b*]thiophene,^[35] 4,7-dibromobenzo[*c*][1,2,5]thiadiazole,^[36] and 2-decyltetradecyl 4-methylbenzenesulfonate^[37] were prepared according to literature procedures. The other materials were commercially available and used as received. All solvents were purified prior to use by distillation.

Thieno[3,2-b]thiophene-3-carbonitrile (1): 3-Bromothieno[3,2-b]thiophene (10.0 g, 45.64 mmol), copper(I) cyanide (10.20 g, 0.114 mol), and quinoline (100 mL) were placed in a 250 mL flask. The mixture was heated at 220 °C under a dry nitrogen atmosphere with stirring at 4 h. After cooling to room temperature, the mixture was extracted with methylene dichloride (3×80 mL). The combined organic layers were dried over MgSO₄ and concentrated. Further purification was carried out by column chromatography on silica gel (*n*-hexane/ethyl acetate, 5:1). Yield: 61.1 % as a yellow solid; ¹H NMR (300 MHz, CDCl₃): δ =7.99 (d, *J*= 1.42 Hz, 1 H), 7.53 (dd, *J*=5.28, 1.42 Hz, 1 H), 7.29 ppm (d, *J*=5.27 Hz, 1 H); ¹³C NMR (75 MHz, CDCl₃): δ =139.8, 139.1, 137.8, 129.7, 119.7, 114.1, 103.7 ppm; MS (EI): *m/z*: 165 [*M*]⁺.

Thieno[3,2-b]thiophene-3-carboxylic acid (2): Compound 1 (7.0 g, 42.36 mmol), potassium hydroxide (10.70 g, 0.191 mmol), and ethylene glycol (150 mL) were placed in a 250 mL flask. The mixture was heated at 195 °C under a dry nitrogen atmosphere with stirring for 12 h. After cooling to room temperature, the mixture was extracted with $2 \times$ HCl and diethyl ether. The combined organic layers were dried over MgSO₄ and concentrated. The compound was further purified by recrystallization from water. Yield: 89.2 %; MS (EI): m/z: 184 [M]⁺.

Thieno[3,2-b]thiophene-3-carbonyl chloride (3): Thieno[3,2-b]thiophene-3-carboxylic acid (2) (6.92 g, 37.56 mmol) and thionyl chloride (70 mL) were placed in a 250 mL flask under nitrogen and heated at reflux for 6 h. After cooling to room temperature and removing the unreacted thionyl chloride by rotary evaporation, compound **3** was obtained as a darkbrown solid. It was dissolved in benzene (180 mL) and used in the next step.

N,N-Dimethylthieno[3,2-*b*]thiophene-3-carboxamide (4): Compound 3 (10.0 g, 49.34 mmol) and benzene (180 mL) were mixed in a 500 mL flask under nitrogen. Dimethylamine (5.56 g, 0.12 mol) was slowly added to the flask. After all of the solution had been added, the mixture was stirred at ambient temperature for 1 h. It was then poured into water (300 mL) and extracted with diethyl ether. The combined organic layers were dried over MgSO₄ and concentrated. The crude product was purified by silica gel column chromatography (*n*-hexane/ethyl acetate, 1:1). Yield: 41% as a dark-brown oil; ¹H NMR (300 MHz, CDCl₃): δ =7.61 (d, *J*=1.51, 1.24 Hz, 1H), 7.48 (dd, *J*=5.28, 1.55 Hz, 1H), 7.26 (d, *J*= 5.28, 1.23 Hz, 1H), 3.21 ppm (s, 6H); ¹³C NMR (75 MHz, CDCl₃): δ = 165.0, 140.0, 138.1, 129.2 m 128.6, 128.3, 118.8 ppm; MS (EI): *m/z*: 211 [*M*]⁺.

FULL PAPER

5,10-Dihydrobenzo[1,2-b:4,5-b']dithieno[3,2-b]thiophene-5,10-dione

(DTBD, 5): Compound **4** (3.90 g, 18.46 mmol) was placed in a well-dried flask with tetrahydrofuran (100 mL) under nitrogen. The solution was cooled in an ice/water bath and *n*-butyl lithium (12.69 mL, 1.6 m in hexane, 20.31 mmol) was added dropwise during 30 min. Then the mixture was stirred at ambient temperature for 30 min. It was then poured into ice/water (10 g) and stirred for several hours. The mixture was filtered and the brown precipitate washed successively with water (200 mL), methanol (50 mL), and THF (50 mL). DTBD (**5**) was obtained as a brown powder. Yield: 1.4 g, 92%; ¹H NMR (75 MHz, CDCl₃): $\delta =$ 7.96 (d, J = 5.28, 1.55 Hz, 2H), 7.75 ppm (d, J = 1.42 Hz, 2H); MS (EI): m/z: 332 [M]⁺.

5,10-Bis(4,5-didecylthiophen-2-yl)benzo[1,2-b:4,5-b']diithieno[3,2-b]thiophene (6): In a nitrogen-purged 100 mL flask, n-butyl lithium (2.5 M in hexane, 42.2 mmol, 16.5 mL) was added dropwise to a solution of 2.3-didecylthiophene (13.6 g, 37.4 mmol) in THF (50 mL) at 0 °C. The mixture was then warmed to 50 °C and stirred for 2 h. Subsequently, DTBD (5; 4.15 g, 12.5 mmol) was added and the mixture stirred for 1 h at 50 °C. After cooling to ambient temperature, a mixture of SnCl₂·2H₂O (11.2 g, 50 mmol) in 10% HCl (30 mL) was added and the mixture was stirred for an additional 1 h. It was then poured into ice/water and extracted with diethyl ether. The combined organic phases were concentrated to obtain the crude product, which was purified by column chromatography on silica gel using hexane as eluent. The compound was further purified by recrystallization from ethanol. Yield: 31.2% as a pale-yellow solid; m.p. 85–86.1 °C; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.47-7.45$ (d, J =5.12 Hz, 2H), 7.31-7.29 (d, J=6.02 Hz, 2H), 7.12 (s, 2H), 2.93-2.70 (m, 8H), 2.17-2.15 (m, 8H), 1.60-1.41 (m, 56H), 0.92-0.89 ppm (m, 12H); ¹³C NMR (75 MHz, CDCl₃): δ = 143.8, 143.4, 142.3, 139.7, 139.6, 134.4, 132.8, 131.4, 130.7, 130.2, 124.7, 120.5, 32.77, 32.71, 31.61, 30.49, 30.43, 30.37, 30.23, 30.15, 30.06, 29.07, 28.78, 23.47, 14.63 ppm; MS (EI): m/z: 1027 [M]+

2,7-Bis(trimethylstannyl)-5,10-bis(4,5-didecylthiophen-2-yl)benzo[1,2-

b:4,5-b']diithieno[3,2-b]thiophene (7): *n*-Butyllithium (2.5 M in hexane, 2.141 mmol, 0.856 mL) was added to a solution of compound **6** (1.0 g, 0.9729 mmol) in THF (30 mL) at 0 °C in a nitrogen-purged flask. The mixture was then warmed to 50 °C and stirred for 2 h at 50 °C and ambient temperature. Subsequently, trimethyltin chloride (1.0 M in THF, 2.14 mL, 2.14 mmol) was added, and the mixture was stirred for an additional 3 h. The mixture was then poured into ice/water and extracted with diethyl ether. The combined organic phases were concentrated to obtain compound **7**. Further purification was carried out by recrystallization from hexane and isopropyl alcohol. Yield: 75.0% as a light-yellow solid; m.p. 104–105.3 °C; ¹H NMR (300 MHz, CDCl₃): δ = 7.32 (s, 2H), 7.13 (s, 2H), 2.96–2.67 (m, 8H), 1.83–1.73 (m, 8H), 1.49–1.31 (m, 56H), 0.92–0.88 (m, 12H), 0.50–0.31 ppm (m, 18H); MS (EI): *m/z* (%): 1353 (100) [*M*]⁺.

5,10-Bis(2-decyltetradecyloxy)benzo[1,2-b:4,5-b']diithieno[3,2-b]thio-

phene (8): DTBD (5; 4.0 g, 12.03 mmol), Na₂S₂O₄ (6.28 g, 36.09 mmol), and tetrabutylammonium bromide (8.53 g, 26.47 mmol) in water (120 mL) were well mixed for 10 min. THF (100 mL) was then added, along with NaOH (20 g). The mixture was then stirred for 2 h at room temperature while purging with nitrogen. 2-Decyltetradecyl 4-methylbenzenesulfonate (18.36 g, 36.09 mmol) was added and the mixture stirred at 60 °C overnight. The solution was then diluted with water (300 mL) and extracted with diethyl ether (200 mL). The organic extract was dried over MgSO4 and the solvent was evaporated. Further purification was carried out by column chromatography on silica gel using hexane as eluent. Yield: 58.5% as a pale-yellow viscous oil; ¹H NMR (300 MHz, CDCl₃): $\delta = 7.64 - 7.62$ (d, J = 5.12 Hz, 2H), 7.39-7.37 (d, J = 3.61 Hz, 2H), 4.27-4.25 (d, J=6.01 Hz, 4H), 2.16–2.06 (m, 2H), 1.71–1.30 (m, 82H), 0.93– 0.88 ppm (m, 12 H); 13 C NMR (75 MHz, CDCl₃): $\delta = 143.8$, 143.4, 142.3, $139.7,\ 139.6,\ 134.4,\ 130.3,\ 120.6,\ 40.14,\ 32.99,\ 30.83,\ 30.47,\ 30.43,\ 30.14,$ 27.69, 23.46, 14.63 ppm; MS (EI): m/z: 1007 [M]+.

2,7-Bis(trimethylstannyl)-5,10-bis(2-decyltetradecyloxy)benzo[1,2-b:4,5-

b']dithieno[3,2-*b*]thiophene (9): *n*-Butyllithium (2.5 M in hexane, 2.18 mmol, 0.873 mL) was added to a solution of compound 8 (1.0 g, 0.9923 mmol) in THF (30 mL) at 0°C in a nitrogen-purged flask. The

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mixture was then warmed to 50 °C and stirred for 2 h at ambient temperature. Subsequently, trimethyltin chloride (1.0 M in THF, 2.18 mL, 2.18 mmol) was added and the mixture stirred for an additional 3 h. It was then poured into ice/water, extracted with diethyl ether, and the combined organic phases concentrated to obtain the crude product. Further purification was carried out by column chromatography on alumina silica gel by using hexane as eluent. Yield: 75.0% as a dark-yellow solid; ¹H NMR (300 MHz, CDCl₃): δ =7.40 (s, 2H), 4.25–4.23 (d, *J*=6.01 Hz, 4H), 2.13 (t, 2H), 2.11–1.20 (m, 82H), 0.92–0.88 (m, 12H), 0.50–0.31 ppm (m, 18H); MS (EI): *m/z* (%): 1333 [*M*]⁺.

Poly [5, 10-bis (4, 5-didecyl thiophen-2-yl) benzo [1, 2-b: 4, 5-b'] dithieno [3, 2-b: 4, 5-b'] dith

b]thiophene-benzo[*c*][1,2,5]thiadiazole] (PDTBDAT-BZ): The polymer was prepared by a palladium-catalyzed Stille coupling reaction. Monomer 7 (0.5 g, 0.369 mmol) and 4,7-dibromobenzo[*c*][1,2,5]thiadiazole (0.1086 g, 0.369 mmol) were dissolved in dry chlorobenzene (7.5 mL). After degassing under nitrogen for 60 min, $[Pd_2(dba)_3]$ (10.14 mg) and $P(\sigma Tol)_3$ (8.9 mg) were added to the mixture, which was then stirred for 48 h at 110°C. 2-Bromothiophene and tributyl(thiophen-2-yl)stannane were injected sequentially into the reaction mixture for end-capping, and the solution was stirred for 6 h after each addition. The polymer was precipitated in methanol and the crude polymer collected by filtration and purified by successive Soxhlet extraction with methanol, acetone, hexane, toluene, and chloroform. PDTBDAT-BZ was obtained by precipitation in methanol. Yield: 85 %; M_n =87000; M_w =188870; PDI=2.14; ¹H NMR (CDCl₃, 500 MHz): δ =8.52–7.96 (br, 4H), 7.74–7.58 (br, 2H), 2.99–267 (br, 8H), 1.60–1.41 (m, 56H), 0.92–0.89 ppm (m, 12H).

Poly[5,10-bis(2-decyltetradecyloxy)benzo[1,2-b:4,5-b']dithieno[3,2-b]thiophene-benzo[c][1,2,5]thiadiazole] (PDTBDOR-BZ): The polymer was prepared by using a palladium-catalyzed Stille coupling reaction. Monomer 9 (0.5 g, 0.374 mmol) and 4,7-dibromobenzo[c][1,2,5]thiadiazole (0.1102 g, 0.374 mmol) were dissolved in dry chlorobenzene (7.5 mL). After degassing under nitrogen for 60 min, [Pd2(dba)3] (10.10 mg) and P-(oTol)₃ (8.67 mg) were added to the mixture and stirred for 48 h at 110°C. 2-Bromothiophene and tributyl(thiophen-2-yl)stannane were injected sequentially into the reaction mixture for end-capping, and the solution was stirred for 6 h after each addition. The polymer was precipitated in methanol and the crude polymer was collected by filtration and purified by successive Soxhlet extraction with methanol, acetone, hexane, toluene, and chloroform. PDTBDOR-BZ was obtained by precipitation in methanol. Yield: 73%; $M_n = 36000$; $M_w = 48240$; PDI = 1.34; ¹H NMR (CDCl₃, 500 MHz): $\delta = 8.52-7.99$ (br, 2H), 7.75–7.58 (br, 2H), 4.25–4.23 (br, 4H), 2.11-1.20 (m, 82H), 0.92-0.88 ppm (m, 12H).

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13248 -

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